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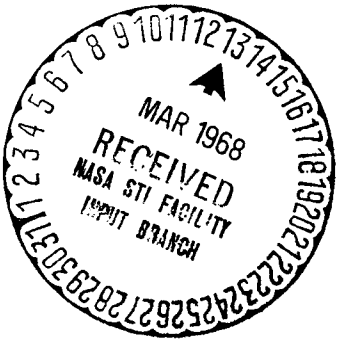

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THE PROBLEM OF ELECTROLYTIC METAL OVERPOTENTIAL

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ABSTRACT. Several characteristics that theoretically arise from the various possibilities of the partial velocity-determining process in electrolytic metal dissociation are discussed. Based on the experimentally-obtained current-voltage curves and the photomicrographs, the role of the active areas is pointed out and a qualitative interpretation of metal dissociation is given.

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Introduction

Electrolytic dissociation of metals, one of the most important and seemingly-simplest electrochemical processes, is a problem that thus far has eluded clarification. The hydrated metal ion ultimately reaches its destination in the crystal lattice of the cathode only after several intermediate states. If all phases of the process continued unhindered, it could be expected that at low current densities the metal electrolysis would proceed without detectable polarization. Polarization would be expected only at current densities causing a noticeable depletion in the solution layer at the cathode. This concentration polarization, all things being equal, depends only on the diffusion coefficient of the electrolyte. For the various electrolyte solutions this diffusion coefficient varies only slightly. Therefore, in metal electrolysis only concentration polarization were at work, on any metal the same current density should cause an approximately equal polarization potential. That, as is well known, is not the case at all. While, for instance, in the case of mercury electrodes the polarization potential reaches the order of 1 mV only at 5-10 mA, similar polarization potentials are found with solid metals under certain conditions already at 100- to 1000-times lower current densities (so-called chemical polarization [1]). Because of the above, the concentration polarization and a perhaps-incidental ohmic potential drop (see below) may amount to the same order of magnitude as that of the mercury electrode under similar conditions; therefore, other causes must be involved.

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To investigate the causes of chemical polarization (here it will be called metal overpotential), examination of current-voltage curves is suggested. Metal overpotential is a function of the low velocity of one of the intermediate partial processes of the dissociation. The shape of the current-voltage curve is thus determined by the kind and voltage-dependency of the velocity-determining

*Numbers in the margin indicate pagination in the foreign text.

action. The shape then, will be indicative of this velocity-determining action.

Causes of Overpotential and the Characteristic of this Action

With regard to the slowest of the overpotential-setting intermittent processes of metal dissociation, the possibility of delayed resupply of free ions from compounds or hydrates was mentioned some time ago. That the dissociation of complexes occasionally proceeds at measurable speeds was directly shown by LeBlanc and Schicht [2]. While the retarded ion resupply from complexes certainly matters in some instances, it does not explain metal overpotential any more than the slow dehydration of ions assumed by Leblanc [1].

Disregarding the solution-determined retardation of ion resupply, the following possibilities in the process of metal dissociation become evident:

1. Metal ion discharge is the slowest step; entry of the discharged ions into the crystal lattice of the cathode proceeds rapidly.

2. The absorption into the crystal lattice, i.e. the electrolytic crystal growth, is velocity-determining; the discharge itself, at the sites where the discharged ions join the lattice, proceeds quickly and without noticeable hindrance.

The current-voltage curves resulting from these possibilities should be noted:

1. If the discharge of the cations is velocity-determining for electrolysis then, as was shown before [3], the following expression applies: /167

$$\eta = a - b \log J \qquad (1)$$

where η is the overpotential, J is the current density, and a and b are constants. This is the well-known case of electrolytic hydrogen dissociation in water.

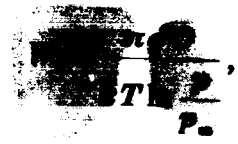
2. If the electrolytic crystal growth is the velocity-determining part, then the shape of the current-voltage curves depends on the type and process of crystal growth. In this case metal dissociation proceeds mainly by forming new planar faces on existing crystals and new seed formation is only of secondary importance. It is conceivable, however, that the growth of the individual small crystals in the planar network is very limited, so that the speed of the metal precipitation and thereby the overpotential also is mainly determined by the frequency of the three-dimensional seed formation. These two possibilities imply different current-voltage curves.

a. If the growth of the crystals plays the important part, two more possibilities arise:

α. Growth velocity is determined by the frequency of two-dimensional seed formation at the crystal faces; the resupply of the growth locations is so fast that the completion from seeds to arrays proceeds without hindrance, i.e. quickly. W_2 represents the work needed for the formation of a two-dimensional seed capable of growth, so that the frequency of seed formation and thereby the current density, in this case proportional to it, by first approximation is:

$$J = k_1 e^{-\frac{W_2}{kT}} \tag{2}$$

Work for two-dimensional seed formation according to Brandes [4] is:



(3)

where ρ determines the specific free boundary energy of the two-dimensional seed, /168
0 the molar surface determinant, p_∞ the vapor pressure of the crystal and p that of the seed. In this case, for the formation of the seed capable of growth, the needed oversaturation p/p_∞ determines the overpotential:

(4)

where n is the valence of the cation.

Therefore,

$$W_2 = \frac{\pi \varrho^2 O}{nF\eta} \tag{5}$$

and

$$J = k_1 e^{-\frac{\pi \varrho^2 O}{kTnF\eta}} = k_2 e^{-\frac{k_2}{n\eta}} \tag{6}$$

(at constant temperature) if the change in boundary energy with potential is disregarded, which is permissible for first approximations, and the constants k_2 are combined.

From this it follows that:

$$\ln J = \ln k_1 - \frac{k_2}{n}\frac{1}{\eta}. \tag{7}$$

In this case then the characteristic is linear when log J is plotted vs. $1/\eta$.

β. The second possibility is the slow resupply to the growth boundaries so that the completion of the planar arrays and thicker layers has a substantial influence on the dissociation velocity. In this case, as Brandes pointed out [5], a linear dependency of overpotential on current density is to be expected. At the boundaries of the individual growth planes and layers the metal dissociation occurs without hindrance. Therefore, the overpotential is zero here. From the surroundings, at polarization potential, a supply of ions then occurs at a current proportional to the polarization potential (Ohm's law). Because dissocation along the edges is fast, the ion resupply in the double layer is eminently velocity-determining and the current of dissociation is proportional to the overpotential.

b. If metal dissociation is determined mainly by the frequency of three-dimensional seed formation, the factor W_3 of three-dimensional seed formation work is sizable. According to Volmer and Weber [6], for spherical fluidic seeds this is: /169

$$W_3 = \frac{16\pi}{3} \frac{\sigma^3 M^2}{d^2 \left(RT \ln \frac{p}{p_\infty}\right)^2}, \tag{8}$$

where σ = specific free surface energy, M = molecular weight and d = density. Using the relation valid for fluids as first approximation for crystals, with reference to Eq. (4),

$$W_3 = \frac{16\pi}{3} \frac{\sigma^3 M^2}{d^2 n^2 F^2 \eta^2} = \frac{k_5}{n^2 \eta^2}, \tag{9}$$

if the potential dependency on σ (as that on ρ above) is disregarded and the constant quantities of k_4 are combined.

It then follows that:

$$J = k_4 e^{-\frac{k_5}{n^2 \eta^2}} \tag{10}$$

and

$$\ln J = \ln k_4 - \frac{k_5}{n^2} \cdot \frac{1}{\eta^2} \tag{11}$$

are characteristic of the process.

To see which of the discussed assumptions is actually valid, the linearity of log J with η, with $1/\eta$, with $1/\eta^2$ or J with η has to be found on the basis of the experimentally-established current-voltage curves. Especially the area of the small overpotential is of interest, since it can be expected that in this area of low oversaturation one of the theoretically-expected curve shapes will appear without interference. With this in mind the current-voltage curves of some metals were examined.

Description of Experiments

Containers for the electrolysis were hermetically sealed with paraffin-coated corks. The metal under investigation served as cathode; the anode was a many-times-larger, cylindrically-bent piece of the same metal. Potential determination of the electrode under investigation was done against a reference electrode of the same material. This reference electrode was in a Luggin capillary /170 whose tip pressed against the electrode under investigation. Current was read on a calibrated galvanometer. The potential difference during electrolysis between the reference and investigated electrodes was determined using Poggendorff's compensation system. To avoid the undesirable polarization of the sample electrode, a Wulff unifilar electrometer served as null indicator. With sufficient temperature protection of the latter, achieved by proper encasement in a cotton-filled box, potential readings with an accuracy of 0.2 mV were feasible. Some readings of the series were taken with a vacuum-tube voltmeter -- to be described elsewhere -- with a sensitivity of 0.1 mV = 1 mm light-pointer deflection.

The experiments were conducted under the exclusion of air in either nitrogen or hydrogen atmosphere. The gases (electrolytic tank hydrogen, tank nitrogen) were scrubbed of oxygen and other impurities in the usual manner. The solutions were respectively nitrogen- or hydrogen-saturated, generaly overnight but at least for two hours before the experiment.

Generally analytically-clean Kahlbaum preparations were used. Otherwise the cleanest available kind was repeatedly recrystallized. Picein putty sealed the electrodes into the glass tubes.

Current-voltage curves for Zn, Cd, Ni, Pb, Bi, Cu and Ag were recorded.

Discussion of Results

Since the primary concern is whether or not and which of the characteristics treated above will coincide with experience at low overpotential, examination of the current-voltage curves centered mainly on this problem. The conclusion of this examination is that none of the three logarithmic characteristics supports the results of the experiments. As a typical example, one of the many attempts (altogether about 200 current-voltage curves of various

conditions were taken) is recounted here. As electrode a zinc sheet electrolytically coated in the same solution with zinc was used; as electrolyte a normal zinc sulfate solution, saturated with hydrogen, was used. From Figs. 1, 2 and 3 it is evident that neither η, $1/\eta$ nor $1/\eta^2$ plotted against log J produces a linear relationship. The near-straightness of the right-hand ends of the $1/\eta$ and $1/\eta^2$ curves must not be construed as an argument for the correctness of the respective equations, because the scale of $1/\eta$ and $1/\eta^2$ expands the curves considerably in these regions. The seemingly-straight portion extends only from 0.1 to 0.3 mV, too narrow a range to draw conclusions. /171

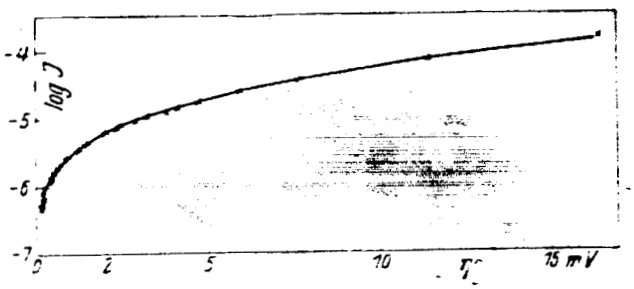


Fig. 1. Zn in Normal $ZnSO_4$ Solution H_2-Saturated (log J - η).

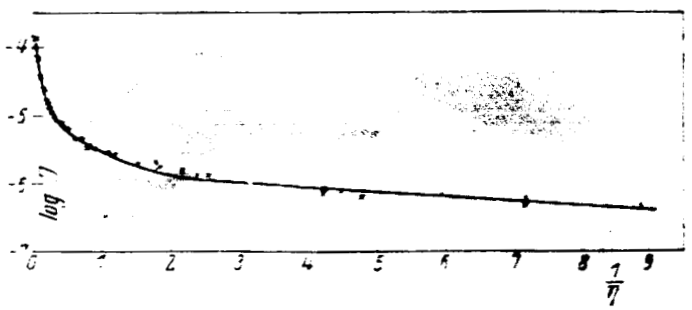


Fig. 2. Zn in Normal $ZnSO_4$ Solution H_2-Saturated (log J - $1/\eta$).

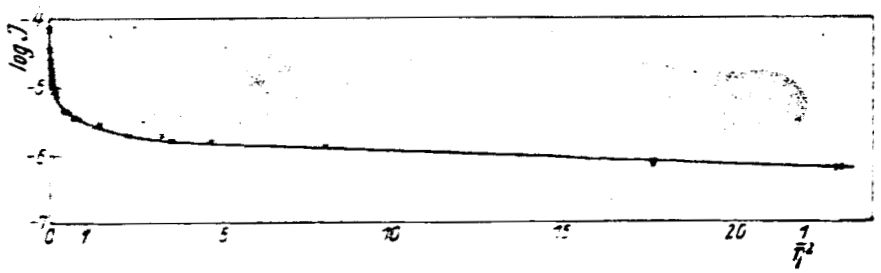


Fig. 3. Zn in Normal $ZnSO_4$ Solution, H_2-Saturated (log J - $1/\eta^2$).

However, if the overpotential is plotted against the current density (Fig. 4), it is evident that the lower parts of the curve between 0.1 and 4 mV are linear. Relations of other metals project similarly. /173

Figs. 4-12 show two current-voltage curves of each investigated metal, the first taken at increasing current densities (x), the other immediately following in the direction of decreasing current densities (o).

In interpreting the current-voltage curves of electrolytic metal dissociation, an important condition has to be considered. Current-voltage curves can give a relatively-simple picture of the electrode process only if size and surface condition of the electrode remains unchanged during the experimental process, as for instance in the case of hydrogen electrolysis. With metal electrolysis, however, this condition is not fulfilled. /174

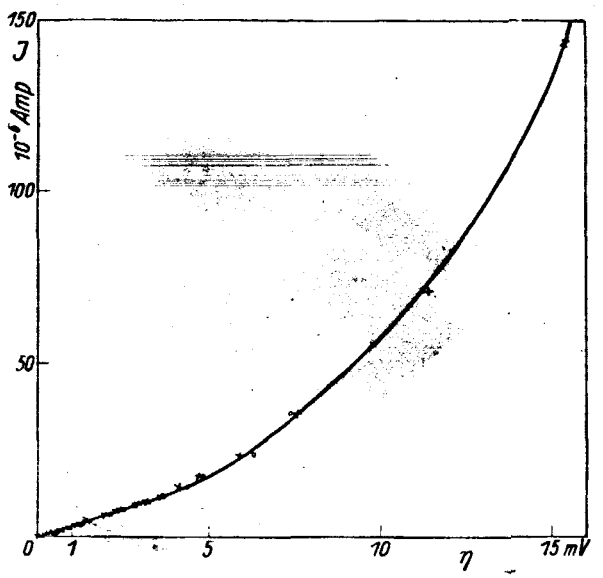


Fig. 4. Zn in Normal $ZnSO_4$ Solution H_2- Saturated (J - η).

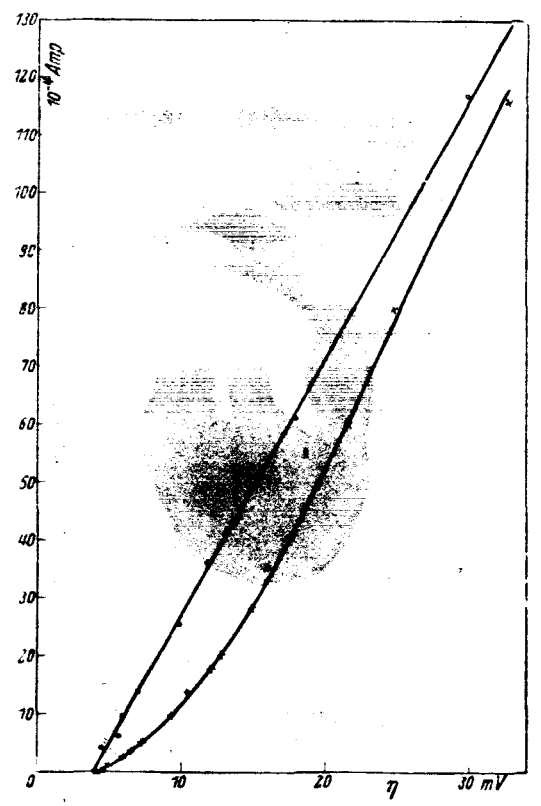


Fig. 5. Cd in Normal $CdSO_4$ Solution, N_2- Saturated

As a result of metal dissociation, both the size of the total surface area and the surface condition changes. This variation in the surface seems to be one of the most important factors that determine the shape of the current-voltage curves.

Performing metal dissociation at low overpotential (low current density), the oversaturation remains low, i.e. the concentration of ions in the double layer is only slightly greater than the equilibrium would demand. Under these conditions metal dissociation does not generally proceed evenly on the whole electrode surface but only in separate active areas. The other /175
regions of the electrode surface do not contribute to the dissociation. Therefore, the actual current density under these conditions is much greater than calculations based on the total surface area would seem to indicate. The latter is not nearly a constant fraction of the former since the number and extent of the active spots change with the oversaturation, i.e. with current density.

Observing electrolytic metal dissociation under the microscope at appropriate magnification and illumination, the discontinuous spotty growth of minute metal crystals is visible, as noted briefly by M. Volmer 7 . Viewing a growing /176
crystal surface at appropriate current, it can be seen that the growth of the surface proceeds in layers. The layer formation starts on one spot of the surface, most frequently in a corner, sometimes on an edge, but never in the center of the surface. The layers then spread across the surface and indeed the faster they spread, the thinner they are. Overlaps create thicker layers whose advance is relatively slowed. With appropriately-directed side illumination the advancing boundaries can be recognized as shadows or as spots of increased reflection (as may be with respect to the relative position of the

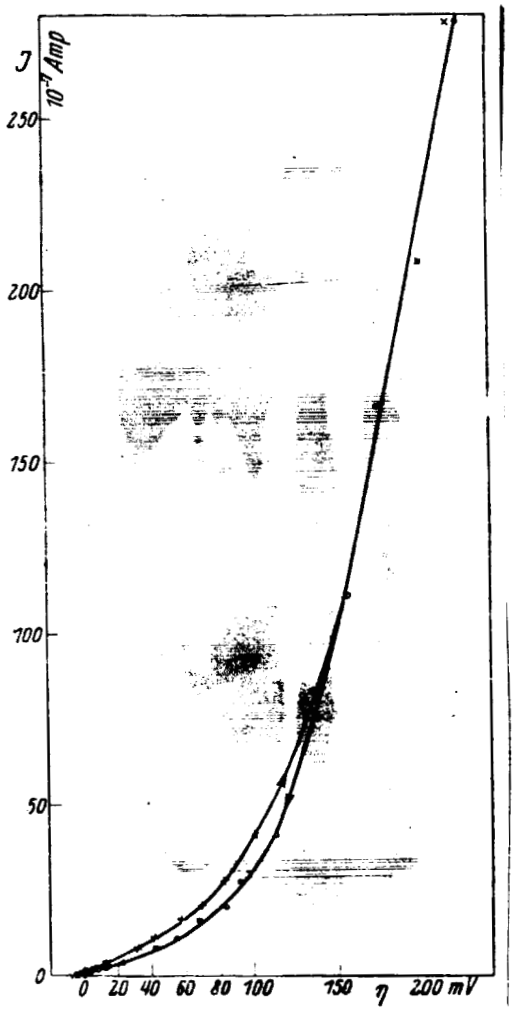


Fig. 6. Ni in Normal Acidic $NiSO_4$ Solution, H_2-Saturated.

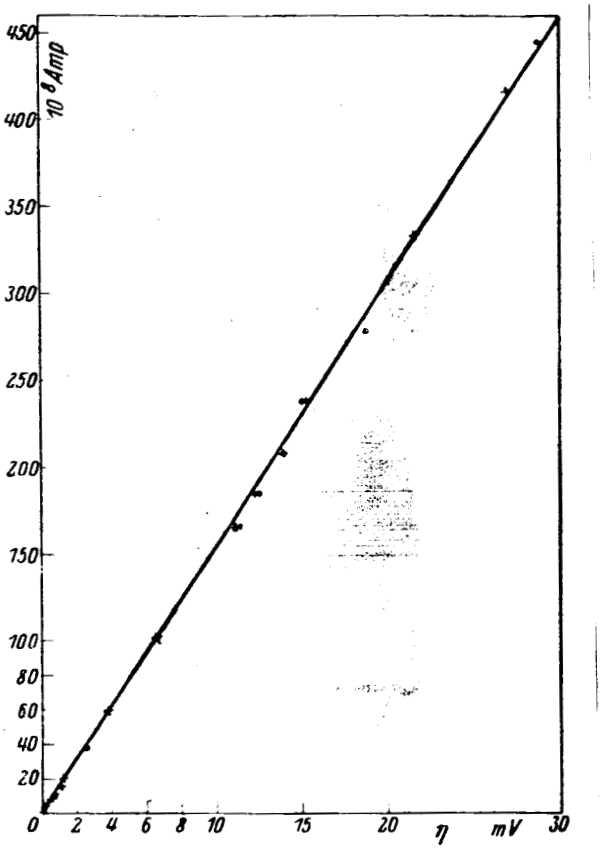


Fig. 6a. Ni in Normal Acidic $NiSO_4$ Solution, H_2-Saturated. The Initial Linear Part in Enlarged Scale.

light source). Fig. 13 shows, at 250-fold enlargement, micrograph sections* of silver dissociation from acetic 2 norm. silver nitrate solution onto a platinum wire at a current of about $3 \cdot 10^{-5}$ amps. Note that on surfaces a and b the formation of new layers in the left corner, one after another and spreading over the surface, is discernible. On surface b the second layer is overtaking the first. As current increases, the steps spread faster and their number increases.

The fact that the formation of new layers begins most often in the corners, seldom on the edges but never in the center of the face stands in agreement with the interpretation of Stranski [8] about electrolytic growth of metal crystals.

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*Professor Lehmann and Dr. Stammreich's valuable assistance is gratefully acknowledged.

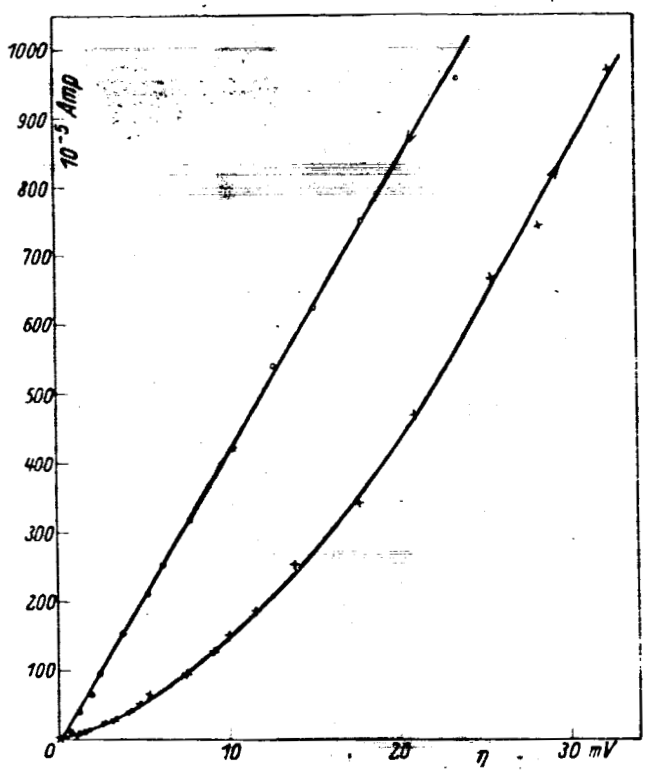

Fig. 7. Pb in Normal Acetic Lead Acetate Solution, N_2-Saturated.

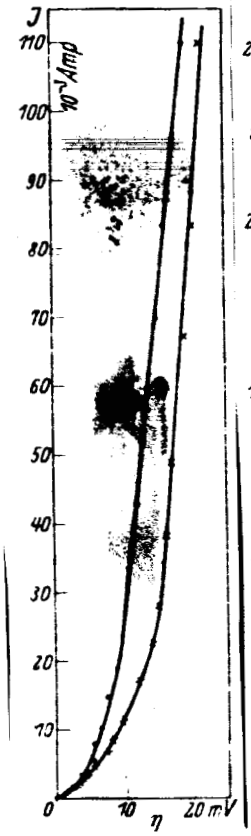

Fig. 8. Bi in Normal Acetic $BiCl_3$ Solution, N_2-Saturated.

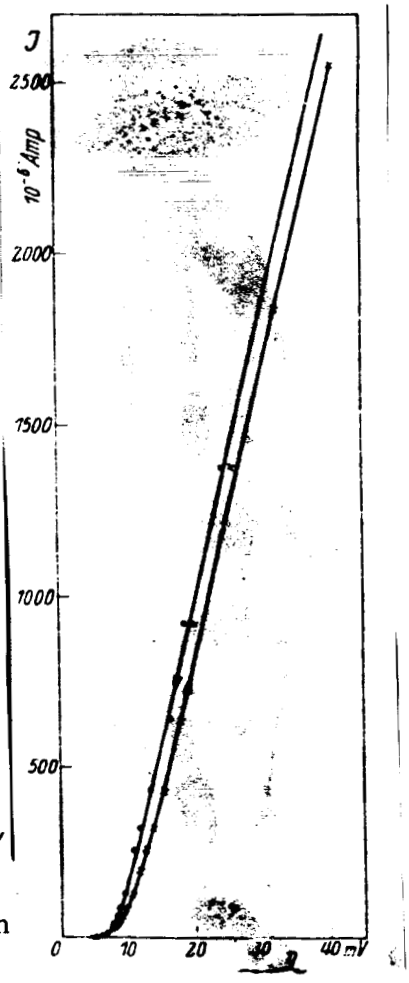

Fig. 9. Cu in Normal Acetic $CuSO_4$ Solution, N_2-Saturated.

In contrast to growth from vapors [9], the electrolytic growth will not start /178
from the centers of the planes* as it should be for homopolar crystals but from the corners or from the edges respectively. The charge density is larger at the edge than in the face centers and even larger in the corners. The increased electrostatic attraction in these areas raises the accumulation energy so that the initial deposition occurs on the corners and edges and the formation of new layers proceeds from here, i.e. the high charge density lowers the boundary energy along here to such an extent that it decreases the work factor of seed formation.

*That in such experiments the seed formation occurs quite regularly in the face centers is not a consequence of energy levels but rather depends on atom migration toward the edges. This atom migration decreases oversaturation more in the boundary zones than in the face centers.

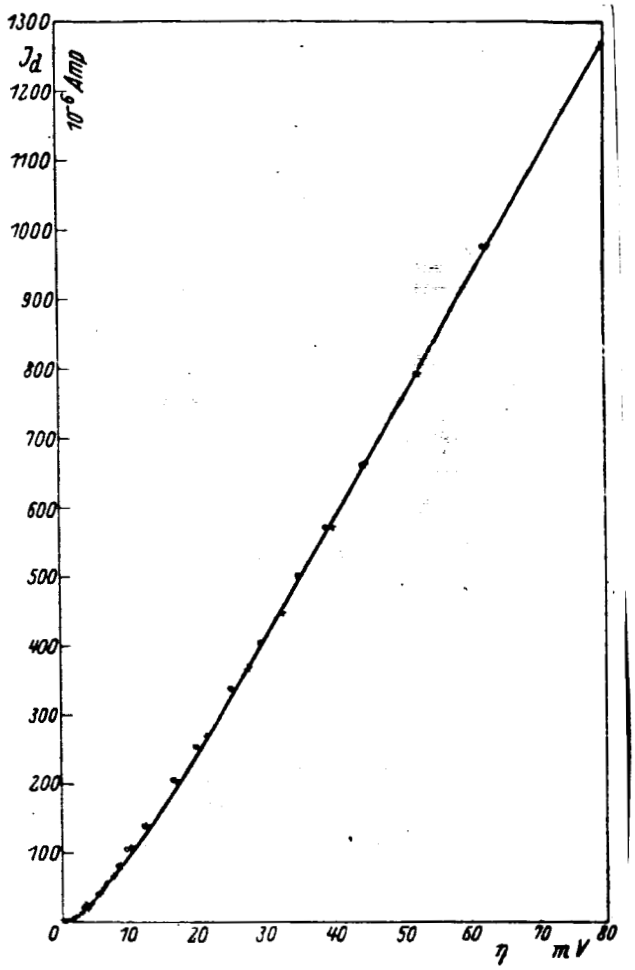

Fig. 10. Ag in Normal Acetic $AgNO_3$ Solution, N_2-Saturated.

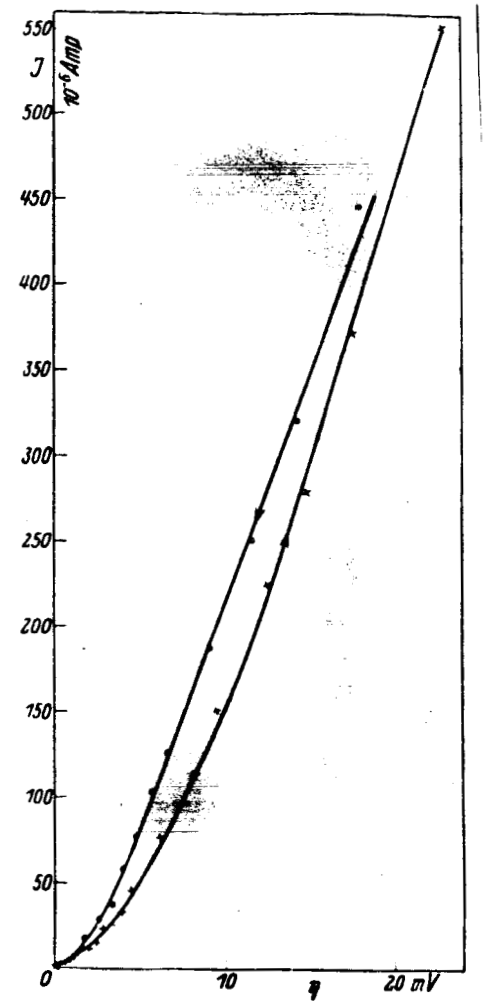

Fig. 11. Ag in $KAgCy_2$ Solution, N_2-Saturated.

A continuous new deposition, however, does not take place -- as the experiment shows -- but the process seems to be quasi-periodic. When the new accumulation leads to the creation of a layer of microscopically-visible thickness, the new growth formation apparently ceases and overrides dissociation on the formed edge, which proceeds with a certain speed and noticeably-constant height across the face. An explanation for this could be found in /179
the dissociation-connected local ion depletion due to which the location of easiest dissociation is no longer the crystal corner with depleted surroundings, but becomes the edge with an undepleted solution environment.

Efforts made to ascertain these optically-established inconsistencies through electrical observation, namely sensitive oscillographic voltage- or current-time curves, were unsuccessful,* showing that initiation of new layers

* Kromrey, using a high-powered amplifier, conducted careful tests ascertain acoustically possible potential oscillations arising from electrolytic

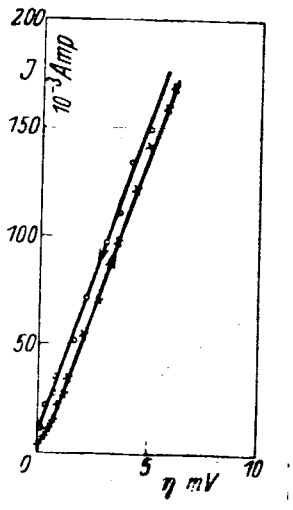

Fig. 12. Ag in Molten $AgNO_3$ (220°C).

in the corners is not opposed by an discernible hindrance in two-dimensional seed formation. This proves the failure of the rule under these assumptions (see pp.2-3). In contrast, seed formation on face centers is so difficult that it does not become noticeable. This difficulty causes the smoothness of the crystal face.

The entire action of electrolysis proceeds therefore through precipitation on the active areas. These constitute a small fraction of the total surface area which grows, however, with rising current density. The assertion that a small part of the surface is active is established first by microscopic observations and second through the agreement with the current-voltage curves. They show after a nearly-linear rise a course that is diametrically opposed to the rate expected for concentration polarization. A linear current-voltage curve could be expected in the case of a point-shaped electrode in not-too-dilute electrolyte solution or melt. The ideal case would be represented by a linear atom chain permitting elongation on one end only. Diffusion there is a fast process so that the consistency of the electrolyte remains constant in the vicinity of the persistently-progressing active area. Then the velocity of the ion resupply is proportional to its effective energy, i.e. a linear dependency exists between current and voltage, like Ohm's law. This ideal case in metal dissociation is approached (particularly with metals of high overpotential) at the smallest current densities by idealizing the electrode through a number of such atom chains according to the majority of active areas. Rising overpotential causes an increase in the periodic boundary-layer formation; the surface shows an increasing roughness. The number of active areas grows with the overpotential which causes the observed quasi-autocatalytic rise of current. This autocatalytic rise, however, must weaken again as soon as the roughness reaches such a high level that a slow-down in the increase rate of active areas takes place. The rise must then become noticeably linear again until finally concentration polarization occurs. /180

The deviation from linearity actually ceases if care is taken that changes in current are not accompanied by changes in the electrode. Such is the case in the behavior of mercury electrodes which yield a linear current-voltage curve, as shown by the experiments of Heyrovsky et al.* and confirmed by these authors, and furthermore by the experiments of Hoekstra [10] where the electrode is continuously scraped. Both cases produce, after initial

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(continued from previous page) crystal growth. Actually, a quiet, characteristic noise was discernible which disappeared upon switching to a mercury electrode of the same size. The low level of this effect made further pursuit appear fruitless. The original purpose, to establish a correspondence between acoustic frequency and the number of surface areas formed per second, was proved particularly impractical.

*See for example, Kemula, Coll. Trav. Chim. Tchechoslov., Vol. 2, p. 397, 1930.

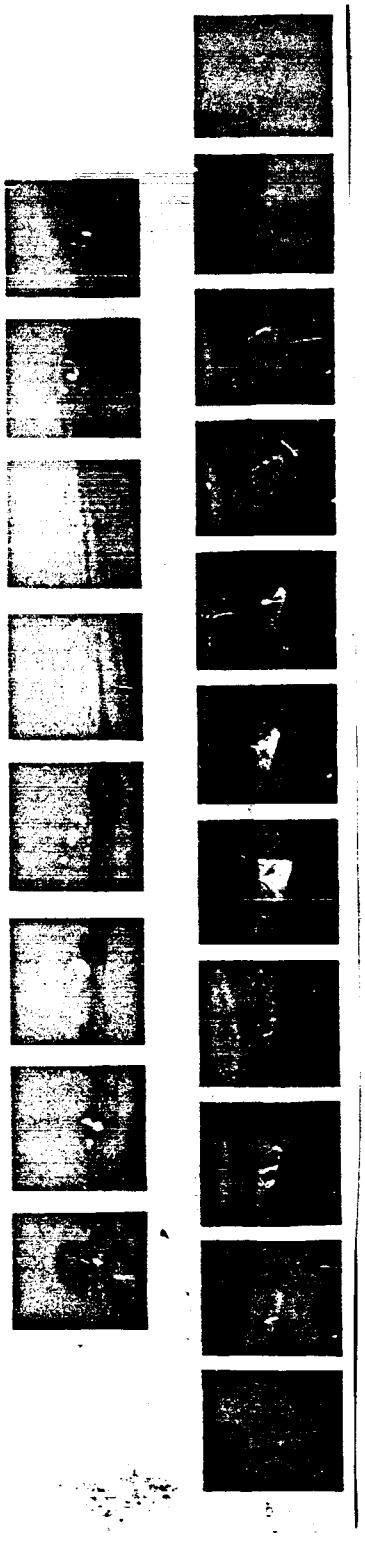

Fig. 13. Microphotographs of Electrolytic Growth of Silver Crystals (x250).

linearity of characteristics, a bending in the direction of concentration polarization, i.e. an opposing bend as with the crystalline metals discussed above.

Summary

Various possibilities exist in the partial process of ion precipitation. For electrolytic metal dissociation this process is velocity-determining. The characteristics of the following cases were treated:

1. The discharging of the ions is velocity-determining. Characteristic: $\log J \sim \eta$.

2. The frequency of two-dimensional seed formation is the slowest event: $\log J \sim 1/\eta$.

3. The frequency of three-dimensional seed formation is the slowest event: $\log J \sim 1/\eta^2$.

4. The outgrowth of seeds in layers is velocity-determining for the dissociation: $J \sim \eta$.

On the basis of current-voltage curves for Zn, Cd, Ni, Pb, Bi, Cu and Ag, examined at low overpotential, and the micrographs of the electrolytic growth of crystals, it was shown that taking into account the changes of the active areas and the total surface, the current-voltage curves can be explained under the assumption that the overpotential is linearly related to the real current density.

Support in performance of this work from the Emergency Committee is gratefully acknowledged.

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